VII.I.2 Microstructural Characterization of Polymer Electrolyte Membrane Fuel Cell (PEMFC) Membrane Electrode Assemblies (MEAs)

Karren L. More
Oak Ridge National Laboratory
1 Bethel Valley Rd.
Oak Ridge, TN 37831-6064
Phone: (865) 574-7788; Fax: (865) 576-5413; E-mail: morekl1@ornl.gov

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

Start Date: FY 1999
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Elucidate membrane electrode assembly (MEA) degradation and/or failure mechanisms by conducting extensive microstructural characterization using advanced electron microscopy techniques comparing fresh and aged MEAs.
- Develop correlations between as-processed MEA microstructure and performance; relate to long-term MEA durability.
- Collaborate with polymer electrode membrane fuel cell (PEMFC) developers/manufacturers to evaluate their MEAs using electron microscopy and complimentary microstructural analysis techniques; provide rapid feedback for MEA optimization.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- A. Durability
- B. Cost
- C. Electrode Performance

Technical Targets

This project is conducting fundamental studies of MEA microstructure and durability, which is being conducted in collaboration with numerous external partners, including MEA manufacturers, PEMFC stack manufacturers, and national laboratories. Insights gained will be applied toward the design and manufacture of MEAs that meet the following DOE 2010 MEA targets:

- Cost: $15/kW
- Durability: 5,000 h
- Total catalyst loading (for both electrodes) : 0.5 g/kW (rated)
- Extent of performance degradation over lifetime : 10%

Approach

- Through established collaborative research projects (non-proprietary and proprietary), prepare thin cross-section specimens from fresh and electrochemically-aged MEAs using the ultramicrotomy technique

developed at Oak Ridge National Laboratory (ORNL). Develop appropriate preparation methodologies for evaluating the many different structural aspects of multi-layered MEAs.

- Use high-resolution scanning, transmission, and analytical electron microscopy (SEM, TEM, and AEM) techniques, as well as other necessary microstructural characterization techniques, to evaluate nm-scale microstructural features and electrochemical-aging-induced structural and microchemical changes within MEA layers (including membrane, ionomer, carbon support, electrocatalyst, and gas diffusion layers).
- Establish correlations between microstructure, performance, and MEA durability.

Accomplishments

- Microstructural changes occurring in Los Alamos National Laboratory (LANL)-produced MEAs were evaluated during life-testing of H_2/air PEMFCs. Extensive Pt (anode) and Pt_3Cr (cathode) catalyst particle coarsening (loss of surface area) and Pt migration into the Nafion® membrane was observed and explained the performance decay observed (loss of 54 mV) during 1,000 h of cell operation. Results were published in an open literature publication.
- Initiated study with LANL to conduct catalyst particle coarsening measurements on electrochemically-aged MEAs using high resolution TEM for comparison with x-ray diffraction studies.
- Developed a new microtomy TEM sample preparation technique, "partial" electrode embedding, for direct imaging of fully intact recast ionomer, carbon/Pt, and pore network within the MEA porous catalyst layers. Results published in an open literature publication.
- Initiated collaborative research with Arkema to evaluate membranes for PEMFCs.
- Completed collaborative study with PlugPower to evaluate microstructural changes occurring during PEMFC stack aging. Reported results during visit to Plug Power.
- Continued collaboration with Fuel Cell Energy to evaluate aging effects during durability testing of MEAs. Have also evaluated new catalyst formulations and support materials for Fuel Cell Energy. Currently evaluating an MEA electrochemically aged using metallic bipolar plates. Reported results during visit to Fuel Cell Energy.
- Continued collaboration with Gore Fuel Cell Technologies to use high-resolution microstructural characterization to evaluate fresh MEA structures for comparison with electrochemically aged MEAs.

Future Directions

- Continue fundamental non-proprietary research with LANL and initiate additional studies on characterizing MEA degradation/aging.
- Improve ultramicrotomy sample preparation technique for studying micro-porous layers and gas diffusion layers.
- Fully evaluate the atomic-scale chemical/compositional properties of Nafion® ionomer (within electrocatalyst layers) and Nafion® membrane before and after durability testing using appropriate high-resolution analysis techniques (such as electron energy loss spectroscopy) and apply these techniques to other membrane (ionomer) compositions.
- Establish new collaborations with industrial partners to conduct relevant MEA durability studies.

Introduction

Proton exchange (or polymer electrolyte) membrane fuel cells (PEMFCs) are being developed for future use as efficient, zero-emission power sources. However, the performance of PEMFCs degrades rapidly with time at operating temperature (currently limited to <100°C) during electrochemical aging. The microstructural characterization project at Oak Ridge National Laboratory (ORNL) has been designed to work with national laboratories and PEMFC developers/manufacturers to evaluate as-

fabricated and electrochemically aged PEMFC MEAs using advanced microstructural characterization techniques in order to establish microstructure-performance relationships and to elucidate MEA degradation and failure mechanisms. Understanding the structural and compositional changes that occur during long-term MEA aging will allow for processing changes required for optimized PEMFC durability and performance.

Approach

In this research, the non-proprietary aspects of MEA evaluation have been conducted in collaboration with LANL. The MEAs were fabricated at LANL using the "thin decal" process. In this process, catalyst inks (a suspension of XC-72 carbon ink, Nafion® ionomer, glycerol, and precious metal catalyst particles) were painted onto Teflon-coated fiberglass substrates (the decal) and heat-treated. Layers of catalyst were sequentially painted and heat-treated until the desired electrode thickness was attained. The decals were then hot-pressed onto both sides of a Nafion® 112 membrane for 5 min. at 205°C. Finally, the decals were peeled off leaving the MEA, which was boiled for 2 h in H_2SO_4 to convert the Nafion® to its proton-conducting form.

Electrochemically-aged MEAs were also supplied by LANL for microstructural characterization. These MEAs were used to study the effect of cycling and temperature on MEA durability under the following conditions:

- 10 mV/sec, 0.1-1.0 V, 1500 cycles, 60°C and 80°C
- 10 mV/sec, 0.1-1.2 V, 1500 cycles, 60°C and 80°C
- 1,200 h drive cycle
- Steady-state operation at 0.6 V for times up to 3,500 h

In these aging studies, TEM was used to determine catalyst particle size distributions within the catalyst layers to correlate with LANL X-ray scattering data.

Bulk MEA compositional and microstructural changes were evaluated before (fresh) and after aging (aged) using backscatter electron imaging and wavelength dispersive spectrometry in a JEOL 8200 electron probe microanalyzer. Transmission electron microscopy using a Philips CM200 FEG-TEM/STEM was also conducted on as-fabricated and aged MEAs. Thin (<75 nm) cross-section MEA specimens were prepared for TEM analysis using room temperature ultramicrotomy (Leica UCT). Details for preparing TEM specimens from PEMFC MEAs have been described previously [1].

Results

There were two primary focus areas for the LANL/ORNL collaborative effort during FY 2005:

1. develop a TEM microtomy specimen preparation technique such that the embedding medium did not interfere with imaging the electrode constituents (i.e., recast ionomer, porosity)
2. identify the MEA microstructural changes which resulted in loss of performance during electrochemical aging (using conditions described above). This is an ongoing (not completed at this point) study, and results will not be presented here.

The performance of a PEMFC degrades during electrochemical aging, primarily as a result of microstructural, compositional, and/or chemical changes associated with the polymer membrane and/or the materials comprising the electrodes. Each of the electrodes in an MEA are composed of several constituents which form interpenetrating, percolating (conducting) networks; a Pt (or Pt alloy) electrocatalyst supported on high surface area carbon material (Pt/C) provides electronic conductivity, a proton conducting ionomer surrounds the Pt/C and holds the carbon support together, and 30-60 vol% porosity provides for gas transport through the electrode. Room temperature (RT) ultramicrotomy (using a Leica UCT) has been used successfully to prepare epoxy-embedded TEM cross-sections from thin (<100 μm), fragile, 3-layer MEAs [1]. When the electrode structure is completely embedded with epoxy, imaging the Pt catalyst particles and carbon support within the electrodes is straightforward. Unfortunately, the presence of epoxy makes it virtually impossible to identify and characterize the continuous ionomer network that surrounds the Pt/C network, which has long been an electrode

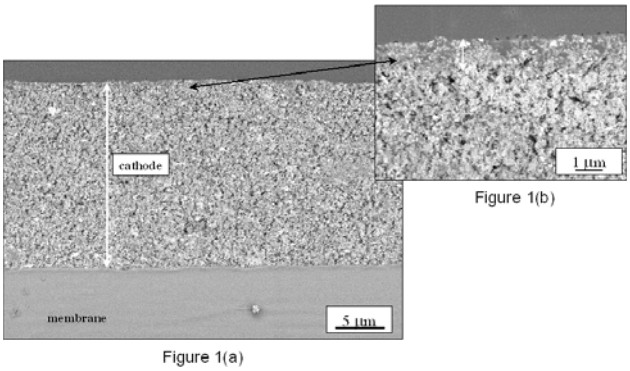

Figure 1. SEM Image of (a) a partially embedded cathode and (b) the epoxy-embedded region at the cathode surface

constituent of primary interest, and to image pore surfaces. An embedding technique was required to "partially" embed the electrode such that the MEA would (1) hold together during RT ultramicrotomy and (2) allow for TEM imaging of unaltered pore surfaces and the ionomer network within the porous electrode.

The best way to start to prepare a partially-embedded electrode structure was to identify a commercial epoxy that was more viscous than those traditionally used for embedding samples for microtomy, which proved to be difficult. Most embedding techniques require an epoxy with a low viscosity to flow and completely fill the pores. Since the electrode structure is open (30-60 vol% porosity), all the epoxies evaluated resulted in fully embedded electrode structures. Partial curing of commercial embedding epoxies was a logical alternative, but was also not successful. Many of the epoxy materials required heat to cure, and when they were removed from the furnace or hot plate after different curing times, the viscosity of the epoxy changed and was difficult to control. The only epoxy that worked consistently for partially-embedding the MEA electrodes, and had an easily-controlled viscosity, was Gatan's G-1 epoxy (not normally used for microtome block preparation but used for traditional TEM sample preparation). To accomplish the partial-embedding of the electrodes, the G-1 was cured until it was slightly red in color (and the consistency of peanut butter). A thin layer was then spread across the top and bottom surfaces of the MEA, encasing it in a hard epoxy shell. The G-1-encased MEA was then set in a mold with Araldite

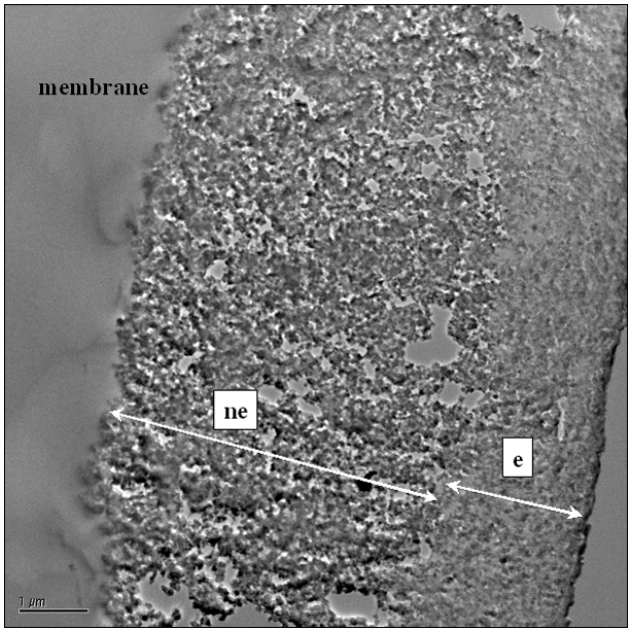

Figure 2. TEM Image of Intact Cathode Showing Epoxy-Embedded Surface (labeled 'e') and Non-Epoxy-Embedded Bulk Cathode (labeled 'ne')

6005 epoxy to prepare a standard block for microtomy (cured at ~60°C for 8 h). SEM cross-section images of a partially-embedded electrode are shown in Figures 1a and 1b. The surface of the electrode is embedded to a depth of ~1-5 µm, enough for the G-1 to "hold on" to the electrode structure and keep it intact during microtomy. The electrode structure below this embedded surface layer is not embedded with any epoxy. A low magnification TEM image of an intact electrode from a microtomed section is shown in Figure 2. The large-scale porosity remains completely intact and can be imaged, as shown in Figure 3, revealing the nature of the pore surfaces, the web-like ionomer network (shown by arrows) within the electrode, and the ionomer thickness and uniformity around Pt/C (Figure 4). This technique is being applied to a variety of MEA systems as part of ongoing research to characterize the microstructure of aged MEAs.

Summary

- Rapid and reproducible preparation of TEM thin sections by ultramicrotomy has been achieved allowing for a greater number of MEAs to be evaluated. In particular, a new technique, "partial" electrode embedding has been

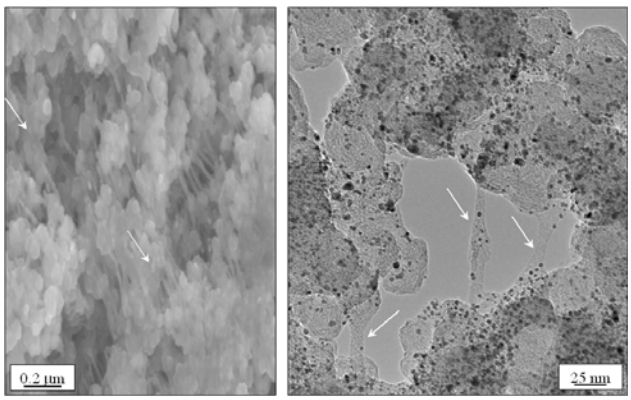

Figure 3(a) Figure 3(b)

Figure 3. (a) SEM and (b) TEM Images of Porosity Within Non-Epoxy-Embedded Electrode Region Showing Pt/C and Web-Like Ionomer Network

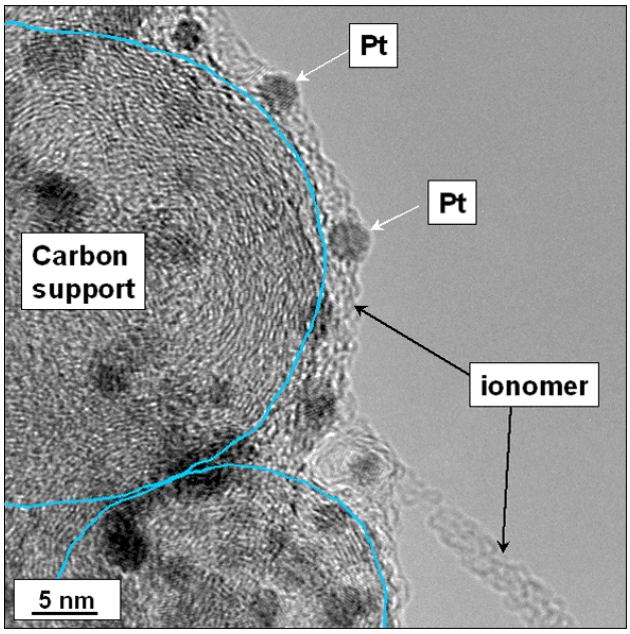

Figure 4. TEM Image of Pt Catalyst Particles on Carbon Support Surrounded by Recast Ionomer (designated by arrows)

developed to image fully intact electrode constituents (specifically the recast ionomer network).

- The new ultramicrotomy preparation technique has been successfully applied to numerous (proprietary and non-proprietary) as-processed and aged MEA structures.
- New insights regarding membrane durability during long-term aging have been achieved; micro-crystallinity and nm-scale compositional changes within aged Nafion® membranes have been observed.
- In addition to the ongoing, non-proprietary research with LANL, several new proprietary studies were established in FY 2005 (Gore Fuel Cell Technologies, Battelle Memorial Institute, Arkema).

Special Recognitions & Awards/Patents Issued

1. K.S. Reeves and K.L. More, The Diatome U.S.A. Award for Excellent Use of Diamond Knives in Ultramicrotomy, 2004.

FY 2005 Publications/Presentations

1. K.L. More, K.S. Reeves, and J. Xie, "Microstructural Evaluation of PEMFC MEAs Using TEM," presented at 2004 Fuel Cell Seminar, San Antonio, TX, Nov. 1-4, 2004.
2. J. Xie, D.L. Wood, K.L. More, T. Zawodzinski, and W.H. Smith, "Influences of Cathode Ionomer Content on PEMFC MEA Structure and Performance," presented at The 206th Annual Meeting of The Electrochemical Society, Honolulu, HI, October 7, 2004.
3. K.L. More, K.S. Reeves, D.L. Wood, and R.L. Borup, "Microstructural Evaluation of Aged PEMFC MEAs," presented at the 107th Annual Meeting of The American Ceramic Society, Baltimore, MD, April 11, 2005.
4. J. Xie, D.L. Wood, K.L. More, P. Atanassov, and R.L. Borup, "Microstructural Changes of MEAs During PEMFC Durability Testing at High Humidity Conditions," *Journal of The Electrochemical Society*, 152(5) A1011-20 (2004).
5. K.L. More and K.S. Reeves, "Partial embedding of 3-Layer MEAs for Ultramicrotomy," in Proceedings of Microscopy & Microanalysis 11(2) (2005). Presented at Microscopy & Microanalysis 2005, Honolulu, HI, August 1-5, 2005.

References

1. D.A. Blom, J. Dunlap, L.F. Allard, and T.A. Nolan, "Ultramicrotomy Sample Preparation of PEMFC Cross Sections," *Journal of The Electrochemical Society* 150 (2003).

2. J. Xie, K.l. More, T.A. Zawodzinski, and W.H. Smith, "Porosimetric Structure of the Membrane Electrode Assemblies Made by Thin Film Decal Method and Its Effect on the Performance of Polymer Electrolyte Fuel Cells," paper submitted to *Journal of The Electrochemical Society* (2004).

3. J. Xie, D.L. Wood, K.l. More, P. Atanassov, and R.L. Borup, "Microstructural Changes of MEAs During Polymer Electrolyte Fuel Cell Durability Testing at High Humidity Conditions," paper submitted to *Journal of The Electrochemical Society* (2004)